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*Title:* Stability of Pu (VI) in synthetic WIPP brines, chloride brines and HCl, HNO3, HClO4 solutions

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*Submitted to:* DOE/Carlsbad Field Office, Carlsbad, NM



**Los Alamos**
NATIONAL LABORATORY

# Los Alamos National Laboratory
# EES-12
# Test Plan, TP 021402, Rev.0
## Stability of Pu (VI) in synthetic WIPP brines, chloride brines and HCl, $HNO_3$, $HClO_4$ solutions

Rev. 0
Effective Date:

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Test Plan for the Stability of Pu(VI) in synthetic WIPP brines, chloride brines, HCl, $HNO_3$, $HClO_4$ solutions, TP 021402, Rev. 0

1.0 APPROVAL PAGE

| | | |
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2.0 TABLE OF CONTENTS

## 3.0 REVISION HISTORY

This is the first version of this test plan (Revision 0, or Rev. 0). If it becomes necessary to revise this test plan, it will be done in accordance with the Los Alamos National Laboratory (LANL) Actinide chemistry program and it will be re-issued in accordance with LANL-EES-12 "Document Control Process." The history of any and all revisions will be described in this subsection.

## 4.0 DEFINITION OF ACRONYMS

CBFO: (U.S. DOE) Carlsbad Field Office.

CCA: (WIPP) Compliance Certification Application.

CEMRC: Carlsbad Environmental Monitoring Research Center

C-INC: (LANL) Chemistry Division (Division)-Isotopes and Nuclear Chemistry

DOE: (U.S.) Department of Energy.

DRC: document review and comment.

EES-12: (LANL) Environmental and Environmental Sciences Division-Carlsbad Operations.

ERDA: (U.S.) Energy Research and Development Administration.

EXAFS: Extended X ray Absorption Fine Structure

ES&H: environment safety and health.

GWB: Groundwater B, synthetic WIPP brine.

I: Ionic Strength.

ILW: Intermediate Level Waste.

LANL: Los Alamos National Laboratory.

LSC: liquid scintillation counting.

m: molal.

M: molar.

MgO: magnesium oxide.

M&TE: measuring and test equipment.

NP: (SNL) Nuclear-Waste-Management-Program procedure.

NWMP: (SNL) Nuclear Waste Management Program.

PA: performance assessment.

PI: principal investigator.

PR: purchase requisition.

Pu: plutonium (oxidation state unspecified).

Pu(III): plutonium in the +III oxidation state.

Pu(IV): plutonium in the +IV oxidation state.

Pu(V): plutonium in the +V oxidation state.

Pu(VI): plutonium in the +VI oxidation state.

Pu(VII): plutonium in the +VII oxidation state.

QA: quality assurance.

QAP: quality assurance procedure.

Rev.: revision.

SCM: (SNL) Software Configuration Manager.

SDR: Sandia-Delegated Representative.

SNL: Sandia National Laboratories.

SP: activity- or project-specific procedures.

STTP: (WIPP) Source-Term Waste Test Program.

TA: Technical Area

TP: test plan.

TRU: transuranic waste.

UV/VIS: ultraviolet/visible (light) spectrophotometry.

WIPP: Waste Isolation Pilot Plant.

WBS: Work Breakdown Structure.

WPO: (SNL) WIPP Project Office.

XRD: X-ray diffraction.

## 5.0 PURPOSE AND SCOPE

Because geological salt formations are considered possible sites for radioactive waste disposal, the effect of radiolysis on high-saline brine under simulated repository conditions has been the subject of numerous investigations within the last two decades (Foerster F. 1917; Allen A. 1952; Lister M. 1956; Rabideau S.W. 1957; Anbar M. 1964; Pourbaix M. 1966; Jayson G. 1973; Thornton A. 1973; Jenks G. 1975; Gilbert G. 1977; Gray W. 1985; Kim J.I. 1985; Kornilov A. 1985; Magirius S. 1985; Buppelmann K. 1986; Kim J.I. 1987; Nagar M.S. 1987; Buppelmann K. 1988; Pashalidis I. 1993; Silber H. 1994; Fukasawa T. 1996; Kelm M. 1999; Kelm M. 2000; Tandon L. 2000; Kelm M. 2001). Also of interest is radiation-chemical behavior in brines, because rock salts in geological repositories generally contain a small amount of brine inclusions that are not homogeneously distributed. Over time, these inclusions may migrate towards the waste container, which acts as a heat source. Brines will also form in geological repositories if the groundwater reaches the salt deposits (Tandon L. 2000).

In the near-field chemistry of a salt repository, the radiolytically-induced redox reactions in concentrated saline solution are of particular importance because the radiolysis of saline solutions results in the creation of oxidizing chlorine species (Anbar M. 1964; Jayson G. 1973; Thornton A. 1973; Jenks G. 1975; Gilbert G. 1977; Zansokhova A. 1977), which may oxidize actinide species to higher oxidation states

(Magirius S. 1985; Buppelmann K. 1986) but also in reducing species such as hydrogen peroxide which may reduce actinide species to lower oxidation states Even though the number of publications concerning the influence of radiolysis by-products on the speciation of actinides is limited, when synthetic brine applications are considered, most of the studies report that hypochlorite generated by alpha irradiation (Kelm M. 1999; Kelm M. 2000) of a concentrated NaCl solution oxidizes Am (III) to Am (V), Pu (IV) to Pu (VI), and Np (IV) to Np (V) (Magirius S. 1985; Buppelmann K. 1986; Kim J.I. 1987; Buppelmann K. 1988; Pashalidis I. 1993; Silber H. 1994; Fukasawa T. 1996). Morgenstern et al. studied the kinetics of the reduction of Pu (V) $O_2^+$ by $H_2O2$ in 1.0 m NaCl solution with time and monitored Pu(V) concentration by ultrafiltration combined with solvent extraction using TTA (Morgenstern A. 1999). The reduction of $PuO_2^+$ was found to be first order with respect to hydrogen peroxide concentration and inverse first order with respect to hydrogen ion concentration.

The primary objective of these experiments is to clarify the complex chemistry of actual TRU waste in contact with WIPP brines as noted in the LANL Source-Term Waste Test Program (STTP) by examining the sub-effects influencing the overall pcH-Eh system. Radiolysis is considered to be the major driving force in oxidation of actinides. Alpha- and gamma-irradiation of chloride solutions (WIPP brine) has the potential to generate secondary oxidizing agents (e.g. hypochlorite, hydrogen peroxide), and further to convert low solubility Pu (III, IV)/Am (III) species to Pu (V, VI)/Am (V) species, which are highly soluble and have a strong tendency for migration in the environment. The temporary appearance of highly mobile plutonium (VI) and (V) species in the STTP experiments might not prove to be important to the WIPP repository concept. Nevertheless, to fully understand and to predict the long-term behavior of actinides under the complex high-saline repository conditions, additional experimental approaches are necessary. The objectives of this research are:

a- The determination of the stability of Pu (VI)-239 in synthetic WIPP brines as well as chloride brine solutions

b- The investigation of the effect of pH on the stability of Pu (VI) in brines

c- The investigation of the effect of $H_2O_2$ ($10^{-2}$ M) on the stability of Pu (VI) in brines at pH 6, 7, 8, and 9.

d- The determination of the kinetics of the reduction of Pu(VI) by $H_2O_2$ and its stability in different concentrations of (1) HCl ($10^{-1}$ M to 5M), (2) NaCl ($10^{-1}$ M to 5M), (3) $HNO_3$ ($10^{-1}$ M to 5M), and (4) $HClO_4$) ($10^{-1}$ M to 5M), solutions under ambient atmosphere at room temperature.

## 6.0 EXPERIMENTAL PROCESS DESCRIPTION

### 6.1 Overall Strategy and Process

LANL personnel will use actinide speciation experiments, and characterization techniques such as UV/Vis spectrophotometry, XRD to determine the influence of alpha-radiolysis by-products on the speciation of Pu (VI) (see Section 5.0, PURPOSE AND SCOPE, above).

LANL personnel will synthesize the brine composition of interest, according to the CEMRC procedure ((Walthall M. 2002).

#### 6.1.1 Experiments

***Task 1 Stability of Pu (VI) in synthetic WIPP brine and chloride brine solutions***

The major chemical in the synthetic WIPP groundwater GWB is $MgCl_2.6H_2O$, but it also contains $Na_2SO_4$, NaCl, LiCl, KCl, NaBr, and $Na_2B_4O_7.10H_2O$. Therefore, it is necessary to compare the stability of Pu (VI) in pure $MgCl_2.6H_2O$ solution and synthetic GWB WIPP brine. Another synthetic WIPP groundwater brine called ERDA-6, where the major constituent is NaCl, will be used to compare the stability of Pu (VI) in ERDA-6 and in a pure 5m NaCl solution. The pH values of $MgCl_2$, NaCl and the two synthetic WIPP brines, ERDA-6 and GWB, are around 7, it is important to know how pH is influencing the stability of Pu (VI) in these solutions. It is also necessary to know the effect of $H_2O_2$ on the stability of Pu (VI) in these 4 solutions at pH relevant for the WIPP repository (i.e. pH 6, 7, 8 and 9). These experiments will provide some useful and

defensible results on Pu (VI) stability under WIPP repository conditions.

The synthetic WIPP brines will be prepared according to the procedure developed by CEMRC (Walthall M. 2002).

The experimental design is described in Table 1.

Table I. Experimental Design for studying the stability of Pu (VI) in Brines

| $MgCl_2.6H_2O$ | 95% GWB synthetic brine | 95% ERDA-6, no $NaHCO_3$ | NaCl |
|---|---|---|---|
| pH 6 | pH 7 | pH 7 | pH 7 |
| pH6 + $H_2O_2$ | pH 7 + $H_2O_2$ | pH7 + $H_2O_2$ | pH7 + $H_2O_2$ |
| pH 7 | pH 8 | pH 8 | pH 8 |
| pH 7 + $H_2O_2$ | pH 8 + $H_2O_2$ | pH 8 + $H_2O_2$ | pH 8 + $H_2O_2$ |
| | | pH 9 | pH 9 |
| | | pH 9 + $H_2O_2$ | pH 9 + $H_2O_2$ |

The experiments will be conducted in duplicate. A total of 40 samples will be analyzed by UV/Vis spectrophotometry over time (10 minutes, 1 day, 10 days, 30 days, 3 months, 6 months, 1 year). Each sample contains 3 mL of $5*10^{-4}$ M of Pu (VI) –239, therefore a total of 14.34 mg of Pu-239 will be used.

The $^{239}Pu$ (VI) stock solution (14.34 mg) will be made up in a final matrix of dilute HCl acid (pH~2).

In a fume hood, the stock solution of Pu (VI) will be opened. With an Eppendorf pipette, the appropriate volume of stock solution will be transferred from the stock solution container to a UV/Vis cell. The volume of Pu (VI) stock solution transferred will correspond to a final activity of 5*10-4 M Pu(VI). Brine solution will be added to Pu (VI) to a total volume of 2.5 mL. The pH will be adjusted to 6, 7, 8, or 9 by adding the appropriate amount of NaOH solution, the proper amount of $H_2O_2$ will be added to the solution. The final volume will be made up to 3mL of Pu (VI) in brine in the UV/Vis

cell. The UV/Vis cell will be sealed for an indefinite period of time (~1 year). The cells will be stored in a small controlled-atmosphere box (10 inch * 10 inch). Periodically, an absorbance UV/Vis spectrum will be taken which implies transferring the sealed UV/Vis cell containing the Pu (VI) in brine ($5*10^{-4}$ M) from the fume hood to the spectrophotometer. The lid of the spectrophotometer will be opened, the UV/Vis cell will be placed in the spectrophotometer. A spectrum will be taken over the wavelength range between 200 nm to 1100 nm using a time period of approximately 1 minute.
When the operation is finished, the UV/Vis cell containing the Pu (VI) solution will be transferred from the spectrophotometer to its original place in the controlled-atmosphere box in the fume hood.

Notes:
Preliminary tests for adjusting the pH of brine solutions have been performed on non-active brine solutions by adding drops of NaOH of different concentrations, by Dr. Mark Walthall from the Carlsbad Environmental and Monitoring Research Center, Carlsbad. The results obtained are as follows:

3.7M $MgCl_2$. $6H_2O$ - pH 7 no precipitate
3.7M $MgCl_2$. $6H_2O$ - pH 8, and 9 precipitate

95% GW-Brine - pH 7, pH 8 no precipitate
95% GW-Brine - pH 9 precipitate

95% ERDA-6 with $NaHCO_3$ - pH 7 no precipitate
95% ERDA-6 with $NaHCO_3$ - pH 8, and 9 precipitate

95% ERDA-6 without $NaHCO_3$ - pH 7, pH 8, pH 9 no precipitate
5M NaCl - pH 7, pH 8, pH 9 no precipitate
These results were used in the conceptual design of the actual experiments (see Table 1).

Task2: Reduction of Pu(VI) by $H_2O_2$ in HCl solutions of varying concentrations

The reduction of Pu(VI) by $H_2O_2$ will be studied in HCl solutions. Table II is describing the experimental matrix.

Table II: Experimental Design for studying the stability of Pu (VI) in HCl

| Sample | HCl (M) without $H_2O_2$ + Pu(VI) ($10^{-3}$ M) | HCl (M) with $10^{-2}$ M $H_2O_2$ + Pu(VI) ($10^{-3}$ M) |
|---|---|---|
| 1 | 0.1 | 0.1 |
| 2 | 0.5 | 0.5 |
| 32 | 1.0 | 1.0 |
| 4 | 2.0 | 2.0 |
| 5 | 3.0 | 3.0 |
| 6 | 4.0 | 4.0 |
| 7 | 5.0 | 5.0 |

The Pu(VI) experiment will require ~5 ml of an 0.01 M Pu(VI) in 0.01 M HCl solution. Total 14 samples will be analyzed by UV Vis spectrophotometer, along with some standards, at the following intervals:

- immediately after addition of Pu(VI)
- after 1 day
- after 10 days
- after 30 days
- 2 months
- 6 months and
- 12 months

If precipitates are formed, the solid sample will be analyzed by diffusion reflectance, XRD and if necessary by EXAFS. During the period of the experiment, ~0.1 ml of solution sample from each tube will be taken for LSC (liquid Scintillation counter) analysis. A 7mL stock solution containing $10^{-2}$ M Pu(VI)-239 in 0.1M HCl (pH = 2) will be prepared at the CMR building. It will be transported from the CMR building to TA 48 facility in the appropriate container via BUS-4. The stock solution containing Pu(VI) 239 will be opened in a HEPA filtered fume hood and the necessary amount of Pu-239 will be transferred in each UV Vis cell containing the HCl solution. The pcH of each sample will

be determined as well as the Eh. The final volume of each sample will be 5 mL with a concentration of Pu-239 of $10^{-3}$ M.

The optical spectroscopy UV/Vis/NIR spectrophotometer will be used to analyze and characterize Pu containing samples. This is the method for characterizing a sample by directing a light beam (conventional light source) into the sample and detecting the response. The various oxidation states of the lighter actinides all have distinct spectra. This makes spectrophotometry uniquely valuable for determining or confirming oxidation state distributions and for assay. Capped absorption cells are used to assure no leakage around the stopper due to capillary action. These cells are filled in a hood, exterior surfaces checked for contamination, placed in a transfer container and taken to the spectrophotometer. The cells are then placed in the cell holder and spectra determined. The cells are returned to the hood via the transfer container. They are stored in a small glovebox (22 cm * 22 cm), placed under a HEPA filtered hood for one year. Once the speciation studies of Pu by UV Vis spectrophotometry are completed, the cells are emptied in a container containing vermiculite for adsorbing the Pu solution. The container will be then disposed. A waste profile form has been set up for this experiment.

***Task3: Reduction of Pu(VI) by $H_2O_2$ in NaCl solutions of varying concentrations***

The reduction of Pu(VI) by $H_2O_2$ will be studied in NaCl solutions. Table III is describing the experimental matrix.

Table III: Experimental Design for studying the stability of Pu (VI) in NaCl

| Sample | NaCl (M) without $H_2O_2$ + Pu(VI) ($10^{-3}$ M) | NaCl (M) with $10^{-2}$ M $H_2O_2$ + Pu(VI) ($10^{-3}$ M) |
|---|---|---|
| 1 | 0.1 | 0.1 |
| 2 | 0.5 | 0.5 |
| 32 | 1.0 | 1.0 |
| 4 | 2.0 | 2.0 |
| 5 | 3.0 | 3.0 |
| 6 | 4.0 | 4.0 |
| 7 | 5.0 | 5.0 |

The Pu(VI) experiments will require 5 ml of an 0.01 M Pu(VI) in nanopure DI water. Total 14 samples will be analyzed by UV Vis spectrophotometer, along with some standards, at the following intervals:

- immediately after addition of Pu(VI)
- after 1 day
- after 10 days
- after 30 days
- 2 months
- 6 months and

9.0 12 months

If precipitates are formed, the solid sample will be analyzed by diffusion reflectance, XRD and if necessary by EXAFS. During the period of the experiment, ~0.1 ml of solution sample from each tube will be taken for LSC (liquid Scintillation counter) analysis. A 7mL stock solution containing $10^{-2}$ M Pu(VI)-239 in 0.1M HCl (pH = 2) will be prepared at the CMR building. It will be transported from the CMR building to TA 48 facility in the appropriate container via BUS-4. The stock solution containing Pu(VI) 239 will be opened in a HEPA filtered fume hood and the necessary amount of Pu-239 will be transferred in each UV Vis cell containing the HCl solution. The pcH of each sample will be determined as well as the Eh. The final volume of each sample will be 5 mL with a concentration of Pu-239 of $10^{-3}$ M.

The optical spectroscopy UV/Vis/NIR spectrophotometer will be used to analyze and characterize Pu containing samples. This is the method for characterizing a sample by directing a light beam (conventional light source) into the sample and detecting the response. The various oxidation states of the lighter actinides all have distinct spectra. This makes spectrophotometry uniquely valuable for determining or confirming oxidation state distributions and for assay. Capped absorption cells are used to assure no leakage around the stopper due to capillary action. These cells are filled in a hood, exterior surfaces checked for contamination, placed in a transfer container and taken to the spectrophotometer. The cells are then placed in the cell holder and spectra determined. The cells are returned to the hood via the transfer container. They are stored in a small glovebox (22 cm * 22 cm), placed under a HEPA filtered hood for one year. Once the speciation studies of Pu by UV Vis spectrophotometry are completed, the cells are emptied in a container containing vermiculite for adsorbing the Pu solution. The container will be then disposed. A waste profile form has been set up for this experiment.

***Task 4: Reduction of Pu(VI) by $H_2O_2$ in $HClO_4$ solutions of varying concentrations***

The Pu(VI) experiments will require 5 ml of an 0.01 M Pu(VI) in 0.1 M $HClO_4$ solution. A total of 14 samples (see Table IV) will be analyzed by UV Vis spectrophotometer, along with some standards, at the following intervals:

- immediately after addition of Pu(VI)
- after 1 day
- after 10 days
- after 30 days
- 2 months
- 6 months and
- 12 months

Table IV: Experimental Design for studying the stability of Pu (VI) in $HClO_4$

| Sample | $HClO_4$ (M) without $H_2O_2$ + Pu(VI) ($10^{-3}$ M) | $HClO_4$ (M) with $10^{-2}$ M $H_2O_2$ + Pu(VI) ($10^{-3}$ M) |
|---|---|---|
| 1 | 0.1 | 0.1 |
| 2 | 0.5 | 0.5 |
| 32 | 1.0 | 1.0 |
| 4 | 2.0 | 2.0 |
| 5 | 3.0 | 3.0 |
| 6 | 4.0 | 4.0 |
| 7 | 5.0 | 5.0 |

If precipitates are formed, the solid sample will be analyzed by diffusion reflectance, XRD and if necessary by EXAFS. The use of hard X-ray absorption spectroscopies are ideal for determining structural data of plutonium at the solid-solution interface, as structural features such as the oxidation state, the presence or absence of the linear trans-dioxo unit, the coordination in the equatorial sphere around Pu(III-VI), and the near neighbor heavy atoms.

During the period of the experiment, ~0.1 ml of solution sample from each tube will be taken for LSC (liquid Scintillation counter) analysis.

A 7mL stock solution containing $10^{-2}$ M Pu(VI)-239 in 0.1M $HClO_4$ (pH = 2) will be prepared at the CMR building. It will be transported from the CMR building to TA 48 facility in the appropriate container via BUS-4. The stock solution containing Pu(VI) 239 will be opened in a HEPA filtered fume hood and the necessary amount of Pu-239 will be transferred in each UV Vis cell containing the $HClO_4$ solution. The pcH of each sample will be determined as well as the Eh. The final volume of each sample will be 5 mL with a concentration of Pu-239 of $10^{-3}$ M.

The optical spectroscopy UV/Vis/NIR spectrophotometer will be used to analyze and characterize Pu containing samples. This is the method for characterizing a sample by directing a light beam (conventional light source) into the sample and detecting the response. The various oxidation states of the lighter actinides all have distinct spectra.

This makes spectrophotometry uniquely valuable for determining or confirming oxidation state distributions and for assay. Capped absorption cells are used to assure no leakage around the stopper due to capillary action. These cells are filled in a hood, exterior surfaces checked for contamination, placed in a transfer container and taken to the spectrophotometer. The cells are then placed in the cell holder and spectra determined. The cells are returned to the hood via the transfer container. They are stored in a small glovebox (22 cm * 22 cm), placed under a HEPA filtered hood for one year. Once the speciation studies of Pu by UV Vis spectrophotometry are completed, the cells are emptied in a container containing vermiculite for adsorbing the Pu solution. The container will be then disposed. A waste profile form has been set up for this experiment.

***Task 5: Reduction of Pu(VI) by $H_2O_2$ in $HNO_3$ solutions of varying concentrations***

The Pu(VI) experiments will require 5 ml of an 0.01 M Pu(VI) in 0.1 M $HNO_3$ solution. A total of 14 samples (table V) will be analyzed by UV Vis spectrophotometer, along with some standards, at the following intervals:

- immediately after addition of Pu(VI)
- after 1 day
- after 10 days
- after 30 days
- 2 months
- 6 months and
- 12 months

Table V: Experimental Design for studying the stability of Pu (VI) in $HNO_3$

| Sample | $HNO_3$ (M) without $H_2O_2$ + Pu(VI) ($10^{-3}$ M) | $HNO_3$ (M) with $10^{-2}$ M $H_2O_2$ + Pu(VI) ($10^{-3}$ M) |
|---|---|---|
| 1 | 0.1 | 0.1 |
| 2 | 0.5 | 0.5 |
| 32 | 1.0 | 1.0 |
| 4 | 2.0 | 2.0 |
| 5 | 3.0 | 3.0 |
| 6 | 4.0 | 4.0 |
| 7 | 5.0 | 5.0 |

If precipitates are formed, the solid sample will be analyzed by diffusion reflectance. During the period of the experiment, ~0.1 ml of solution sample from each tube will be taken for LSC (liquid Scintillation counter) analysis.

A 7mL stock solution containing $10^{-2}$ M Pu(VI)-239 in 0.1M $HNO_3$ (pH = 2) will be prepared at the CMR building. It will be transported from the CMR building to TA 48 facility in the appropriate container via BUS-4. The stock solution containing Pu(VI) 239 will be opened in a HEPA filtered fume hood and the necessary amount of Pu-239 will be transferred in each UV Vis cell containing the $HNO_3$ solution. The pcH of each sample will be determined as well as the Eh. The final volume of each sample will be 5 mL with a concentration of Pu-239 of $10^{-3}$ M.

The optical spectroscopy UV/Vis/NIR spectrophotometer will be used to analyze and characterize Pu containing samples. This is the method for characterizing a sample by directing a light beam (conventional light source) into the sample and detecting the response. The various oxidation states of the lighter actinides all have distinct spectra. This makes spectrophotometry uniquely valuable for determining or confirming oxidation state distributions and for assay. Capped absorption cells are used to assure no leakage around the stopper due to capillary action. These cells are filled in a hood, exterior surfaces checked for contamination, placed in a transfer container and taken to the spectrophotometer. The cells are then placed in the cell holder and spectra determined. The cells are returned to the hood via the transfer container. They are stored

in a small glovebox (22 cm * 22 cm), placed under a HEPA filtered hood for one year. Once the speciation studies of Pu by UV Vis spectrophotometry are completed, the cells are emptied in a container containing vermiculite for adsorbing the Pu solution. The container will be then disposed. A waste profile form has been set up for this experiment.

### 6.2 Planning and Quality Assurance

LANL personnel will carry out the work described in this test plan in accordance with SNL/WIPP NPs, formerly known as QAPs or LANL Standard Operating Procedures (SOPs) or project-specific procedures. If project specific procedures are developed, LANL Document Control program will be ised to prepare and control them as designated procedures.

Each LANL individual performing work under this test plan is responsible for achieving and maintaining quality. LANL line management is responsible for verifying quality. Independent LANL, SNL, and/or DOE/CBFO assessors are responsible for ensuring that quality is adequate for the intended use and properly documented.

LANL personnel will plan and document the processes used for the experiments described in Subsection 6.1, Overall Strategy and Process (see above), in accordance with the NP 20-2, "Scientific Notebooks." If project-specific procedures are developed, Known sources of error and uncertainty, including any uncertainty about the quality of input data, and the compatibility of data processing with any conceptual/mathematical models used at each applicable stage will also be documented in the scientific notebook. Documents to be maintained as QA records (e.g. scientific notebooks) that are not already specified in this test plan will be specified in the appropriate procedures.

LANL will control documents, as appropriate, in accordance with NP 6-2, "Document Control Process."

LANL will control processes such as performing analyses, checking routine mathematical calculations, or verifying spreadsheet calculations or utility codes to ensure that these processes are accurate, consistent, and reproducible.

LANL will develop, document, review, and approve any software developed or adapted for the WIPP project that performs data reduction or analysis, and/or supports

models, and whose results are used in support of the WIPP in accordance with NP 19-1, "Software." (LANL may document simple analyses according to the requirements specified in NP 9-1, "Analyses.") They will list software classified as "off-the-shelf" or "vendor" software, data-acquisition software, and other classifications in their QA records. They will also list software classification, version, and platform and approved users in their QA records. In addition, they will submit the list to the SNL/WIPP Software Configuration Manager (SCM) for inclusion on the WIPP Software Baseline Inventory List. (They can obtain the name and address of the current SCM from the Sandia-Delegated Representative, or SDR.)

LANL will identify conditions adverse to quality, determine the cause of these conditions, correct them, take actions to prevent recurrence, and document all of these steps.

LANL personnel working in collaboration with CEMRC will identify, label and control all samples in accordance with CEMRC CP-PROC-0003-000 "Logging Research Samples into the SID database". They will transfer all samples in accordance with CEMRC CP-PROC-001-000-100898 "Procedure: Sample Tracking and Chain of Custody" or CEMRC CP-PROC-005-000 "Analytical Request From Procedure".

### 6.3 Sample Control

The experiments described in Subsection 6.1, Overall Strategy and Process (see above), will require some sampling of solutions and solids for post-test characterization. LANL personnel will identify, label, and control all samples in accordance with NP 13-1, "Sample Control." They will transfer all samples in accordance with SP 13-1, "Chain of Custody."

P. Paviet-Hartmann and N. Lu, the LANL Principal Investigators (PIs) responsible for the work described in this test plan, will determine the disposition of samples after this work is completed.

6.4 Data Quality Control

LANL personnel will implement a calibration program for all of the measuring and test equipment (M&TE) used for the experiments described in Subsection 6.1, Overall Strategy and Process (see above), in accordance with NP 12-1, "Control of Measuring and Test Equipment." This M&TE calibration program will meet the requirements in NP 12-1 for: (1) receiving and testing M&TE; (2) technical operating procedures for M&TE; (3) the traceability of LANL standards to nationally recognized standards such as those from the National Institute of Standards and Technology; and (4) maintaining calibration records.

6.5 Data Identification and Use

LANL personnel will use scientific notebooks to record all of the data and conclusions obtained from the experiments described in Subsection 6.1, Overall Strategy and Process (see above), in accordance with NP 20-2, "Scientific Notebooks." Data transfer and reduction controls, control of erroneous or inadequate data, including identification, segregation and disposition of the data, and data conversion controls will be documented in the scientific notebook or in a project-specific procedure (SP).

LANL will check the results of calculations in accordance with NP 9-1, "Analyses." They will use one of the following methods: (1) separate independent calculations using the same or different analytical methods as the original calculations; (2) a check of each of the calculation steps in the original calculations, or a random (spot) check of the original calculations.

6.6 Records, Reports, and Audits

LANL personnel will consider all records providing evidence of quality, including but not necessarily limited to personnel qualification and training forms, lists of M&TE and software, technical procedures, laboratory notebooks, calibration records, and

reports, to be QA records. All of these records will be accurate, complete, identifiable, and legible.

## 7.0 TRAINING

P. Paviet-Hartmann and N. Lu, the LANL PIs responsible for the work described in this test plan, will ensure that training of LANL personnel is assigned and completed, and that the certification of personnel qualifications is documented according to the Hazard Control Plan LANL-EES 12 HCP. LANL personnel will complete all personnel qualification and training, and all of the documentation thereof, before beginning work.

## 8.0 HEALTH AND SAFETY

The work described in this test plan will require that LANL personnel use small quantities of Pu. Handling Pu, and other actinide elements in the laboratory, even in small quantities, necessitates specialized requirements for facilities, procedures, training, and oversight. These environment safety and health (ES&H) requirements are even more demanding than those necessary for most other chemical elements.

LANL has extensive experience handling Pu, and other actinide elements, and has developed comprehensive, detailed ES&H requirements and standard operating procedures for such work. Description of these requirements and procedures is beyond the scope of this test plan. All LANL personnel will work under Hazard Control Plans (HCPs) for the appropriate locations where work is performed at LANL sites. All personnel will be qualified and approved to work by the appropriate LANL line manager (Group Leaders of EES-12 and C-INC).

However, it is worth noting that, in the context of LANL's experience with Pu, and other actinide elements, the quantities of Pu LANL personnel will use for this work are small, and the procedures they will use are routine. Consequently, there are no special licensing or permitting requirements required (see 9.0, LICENSING/PERMITTING, below).

## 9.0 LICENSING/PERMITTING

There are no licensing or permitting requirements specific to the work described in this test plan (see 8.0, HEALTH AND SAFETY, above).

## 10.0 DELIVERABLES

The expected deliverables for the investigation on the " Stability of Pu (VI) in synthetic WIPP brines, chloride brines and HCl, $HNO_3$, $HClO_4$ solutions" are:

- Quaterly progress reports providing experimental updates
- Final report on " Stability of Pu (VI) in synthetic WIPP brines, chloride brines and HCl, $HNO_3$, $HClO_4$ solutions"
- Journal publication for Tasks 1, 2, 3, 4 if deemed worthwhile

## 11.0 REFERENCES

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